

1388581

- (21) Application No. 25938/72 (22) Filed 2 June 1972
(31) Convention Application No. 2127618 (32) Filed 3 June 1971 in
(33) Germany (DT)
(44) Complete Specification published 26 March 1975
(51) INT CL² C12C 9/02
(52) Index at acceptance C6E H



(54) METHOD OF PRODUCING HOP EXTRACTS

(71) We, HAG AKTIENGESSELLSCHAFT, a German Company of Hagstrasse, 28 Bremen, Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method of producing hop extracts.

For a long time it has been increasingly customary to use hop extract instead of natural hops for brewing purposes. Hop extracts have a number of advantages, particularly in respect of price but also in respect of the process technology of brewing and the quality of the beer. Thus a large number of publications have appeared dealing with the production of hop extracts, in substantially all of which the resin components and essential oils of the natural hops are first extracted with organic solvents. For this purpose use is generally made of halogenated hydrocarbons, such as methylene chloride, carbon tetrachloride, trichloroethylene, as well as for example methanol, ethanol, acetone or n-hexane, either alone or in admixture. In these processes the pure resin components and ethereal oils of the hop are primarily extracted, but also, depending on the polarity and selectivity of the solvents, also some of the tannin matter and the like. Some methods also work with mixtures of organic solvents and ammoniacal aqueous solutions in order to extract resin components and tannin in one operation. Later methods also extract from the outset with water, the aqueous solution containing isomerisation products then being used for brewing purposes.

The procedure, however, frequently comprises extracting mainly or exclusively the resin components in the first extraction step, whereupon, after steaming to drive off the solvents contained in them, the spent hops are subjected to a second extraction with water. The solvent extracts and water extracts are then combined to form the finished hop

extract. In addition, the pure solvent extracts, i.e. the resin components largely free from tannin, are also used by themselves for brewing purposes, and in this case it has been found that these lead to particularly good froth stability of the beer, while at the same time the colour, cold stability, and taste differ only slightly from beers produced with extract containing tannin, (H. Schilfarth, *Mschr. Brauerei* 18, 65—77, 1965).

Processes known hitherto have the common disadvantage that the extraction solvents must be removed from the hop extracts and also from the spent hops. In the case of the hop extracts this removal can be done only incompletely, since these are syrupy or pasty masses which give up the residues of solvent only very reluctantly. Moreover, the chemical influence of the solvent on the substances contained in the hops is in many cases nuclear. In any case the detection and removal of solvent residues in the extract was and continues to be pursued with considerable technical and scientific effort, since particular attention has to be devoted to this problem owing to legal purity requirements. Another disadvantage of prior art processes is that the composition of the extract varies in dependence on the solvent.

The present invention provides a method of producing hop extracts which may or may not contain tannin, wherein all the disadvantages of previous methods, such as solvent residues in the extract, the formation of toxic substances, and different extract compositions, etc. are eliminated or at least minimised.

The invention is based on the observation that carbon dioxide or other solvent gases which is supercritical in respect of both pressure and temperature is a good solvent medium for the resin components and essential oils contained in hops, and in addition is entirely unobjectionable from the health point of view.

According to the invention, there is provided a method of producing hop extracts from hops by extraction with a solvent in

which air-dry hops are extracted with a gas which is supercritical in respect of both pressure and temperature and which is unobjectionable from the point of view of health, said gas comprising SF_6 , CHF_3 , CHF_2Cl , CF_3Cl , $\text{CF}_2=\text{CH}_2$, C_2F_6 , N_2O , ethane, ethylene or CO_2 or mixtures of any two or more thereof, the extract being thereafter separated from the resulting solution by lowering the pressure to below the critical pressure.

Supercritical gases, i.e. gases above the critical temperature and above the critical pressure, constitute a separate phase which differs clearly from the normal gas phase. In respect of the spacing of the molecules from each other and therewith the density and the solvent power, the supercritical phase is similar to a liquid while it corresponds to a normal gas in respect of mobility. On account of their solvent power, which is similar to that of a liquid, gases in the supercritical state can be designated as solvents.

Carbon dioxide is particularly preferred as the extraction medium, but it is also possible to use the other said solvent gases and the N_2O is preferably isosteric with CO_2 . Before use, these gases should desirably be purified.

The entire soft resin and the essential oils of the hops but less than 100% of the hard resin fraction may be extracted by use of extraction pressures of from 100 to 220 atmospheres gauge.

For producing a hop extract containing tannins the hops are extracted with a supercritical gas, the residue is extracted with water in a known procedure, the latter extract dried and mixed with the first extract obtained by extraction with supercritical gas.

Extraction with liquid CO_2 is also possible, but the dissolving power of the latter is lower than that of the supercritical medium, and this also applies to the other gases mentioned above. Nevertheless the dissolving power changes abruptly when the gas passes into the supercritical state and is then considerably greater. Where the hop extract of the method of the invention is to contain less than 2% water, a temperature above the critical temperature is maintained during the separation.

By way of example, a specific embodiment of the invention will now be described with reference to the accompanying drawing which shows, diagrammatically, the apparatus employed. The embodiment involves the use of carbon dioxide as the extraction solvent gas, but it is to be understood that other suitable solvent gases, for example those listed above, or mixtures thereof could be used in place of the carbon dioxide, appropriate changes being made to take account of different critical pressures and temperatures of such a solvent gas.

In a preferred embodiment of the inven-

tion, which is illustrated in the accompanying drawing, the operation is carried out as described below.

The gas used is stored in a tank 1 controlled by a valve 2. The hops are contained in a pressure tank 13 which is equipped with a heating jacket 14. The entire system is first flushed free of air with dry CO_2 . For the actual filling operation (with CO_2), valves 2, 6, 5, 3 and 7 are opened. All other valves are closed. Due to the valve 5 also being open, a certain amount of CO_2 flows from the tank 1 into the tank 15. The CO_2 , which is to begin with liquid, is then pumped out of the tank 1, by a pump 11 and flows through a heat exchanger 12 where it is brought to supercritical conditions of pressure and temperature.

The resulting gas flows further into a tank 13 and the pressure therein increases until the correspondingly adjusted throttle valve 4 opens. The essential oils and resins are dissolved out of the hops contained in the tank 13 by the compressed gas so that a solution results which, although still having the character of a gas in respect of compressibility, is already similar to a liquid in respect of its density. This is herein called a "supercritical solution". Once the pressure to which the valve 4 is adjusted is reached, that valve opens, allows a certain amount of supercritical solution to pass through and closes again when the likewise adjusted lower pressure limit for the tank 13 is reached. The valve 6 is closed after the first response of the valve 4. Due to the expansion at the valve 4 into the tank 15 which is equipped with a jacket 16 for heating or cooling, the supercritical solution separates and the dissolved hop components precipitate, that is a two-phase system CO_2 /hop extract is now present. This separation effect comes to be because gases have a greater solvent power at higher pressures than at lower pressures. If the temperature in the tank 15 is below the critical temperature of the gas, liquefaction takes place if care is not taken that a corresponding amount is present in the tank, 15. That is, however, the case because, as stated at the outset, the valve 5 was also initially opened. If the temperature in the tank 15 is above the critical temperature of the gas, the gas will not liquefy but the dissolved hop components, nevertheless, precipitate on account of the lower pressure. Due to this process method, the hop extract in the tank 15 has a lower water content because in that case not as much water is separated. The reason for that is that supercritical gas in spite of lower pressure takes up relatively more water than the liquefied gas. The gas now free of extract is drawn off from the tank 15 by suction, liquefied in a heat exchanger 16 and recycled by the pump 11. If a pump for liquefied gases is not to be used

but a compressor which can convey and compress only gases, the function of the heat exchanger 16 changes to the effect that in this case the gas is now preheated to supercritical temperatures while the heat of compression is conducted off in the heat exchanger 12.

When the extraction is completed, the CO₂ is pumped back into the tank 1. The gas is liquefied in the heat exchanger 16. The valves 7, 18, 10, 2 and 5 are opened. All others are closed. Care is, however, taken that a small residual amount of liquid CO₂ remains in the tank 15. After the CO₂ thus having been substantially evacuated from the plant, the remaining gas is from the tank 15 drawn off from the vapour phase by suction so that the temperature drops to -10°C. The hop extract is thereby so solid that it can be removed by mechanical scrapers. It still contains a certain amount of CO₂, which during the subsequent heating and storage at about 0°C gradually evaporates and at the same time serves as an inert gas atmosphere for the material which is sensitive to air.

Substantially all the resin in the hops can be extracted quantitatively and analysis of the CO₂ extract shows in addition to water it contains substantially only the resin components. It is a particular feature of the process that the acids, which are important for the bitter principles, can be removed quantitatively from the hops, while the β fraction and the hard resins can likewise be removed either completely or only to a certain extent, and here again differentiations between the last two components mentioned are also possible. It is thus possible to produce extracts with particularly high α -acid contents.

Thus, in a preferred embodiment of the invention the entire soft resin fraction and the essential oils of the hops but less than 100% of the hard resin fraction can be extracted, by working with extraction pressures from 100 to 200 atmospheres gauge.

According to another preferred embodiment of the invention all the α -acids and the ethereal oils but less than 100% of the β -acids contained in the hops and also less than 100% of the hard resin components are extracted by working at extraction pressures of 100—220 atmospheres gauge and further separating the resulting extract by subjecting it to a further supercritical extraction at pressures of 100—150 atmospheres gauge.

The product obtained according to the invention is a paste varying from light to dark green in colour, the colour depending on the extraction temperature; it is substantially free from tannin matter (see analysis) and can be used directly for brewing purposes, unless it is preferred to mix it with the hop components obtained by aqueous extraction.

The extracted hops are substantially lighter

in colour than before the treatment and are practically odourless. This point is particularly important for subsequent aqueous extraction of the treated hops, since above all the readily volatile constituents of the ethereal oil can no longer be lost during the water extraction and subsequent vacuum concentration.

The hops freed from all the resin and from the ethereal oils can then be extracted in the aqueous phase in known manner without further pre-treatment, the solution concentrated, and the residue combined with the CO₂ extract in suitable mixers in an atmosphere of inert gas.

In another modification of the process the hops freed from all the resin and from the essential oils by treatment with dry supercritical CO₂ may, instead of being processed direct with water, first be processed in a second step with supercritical CO₂, which in this case is moist. (The gas current, controlled by valves 8 and 9, is moistened in the tank 19). An extract fraction the components of which already have, for example, something of the character of tannin is thereby obtained. The resulting extract, which once again may at choice be either substantially dry or contain water, is mixed with the extract obtained from the first step and then either used by itself or the extract fraction which is obtained from the purely aqueous extraction (3rd step), and which may for example be spray or freeze dried, is likewise added.

As already mentioned, for the supercritical extraction it is necessary to work at pressures above $p_{crit., gas}$ and at temperatures above $t_{crit., gas}$. In practice values above 100 atmospheres gauge, preferably 150—400 atmospheres gauge, are selected where pressure is concerned. In respect of temperatures, guidance is supplied by the thermal loadability of the material, that is to say the lowest possible temperatures will be selected here, for example in the range between 32 and about 100°C, preferably between 40 and 50°C.

Examples

1. 1 kg of air-dry Hallertau hops were processed in the installation illustrated in the drawing under the following conditions with dry CO₂:

Extraction pressure $p_1=315$ atmospheres gauge

Mixture separation pressure $p_2=67$ at. gauge.

Extraction temperature $t_1=50^\circ\text{C}$,

Mixture disintegration temperature $t_2=25^\circ\text{C}$.

Time: 7 hours.

Total amount of CO₂ circulated: 49.6 kg.

Result:

170 g of a water-containing olive green,

pasty extract were obtained. The residue of extracted hops was yellowish light green in colour and substantially odourless.

- 5 The hops freed from resin components were then, without further pre-treatment, extracted for three hours with 10 litres of water in a water bath at 90–95°C., the spent hops were filtered off and the solution concentrated in vacuo at 40–50°C bath

temperature until the residue had a syrupy consistency. After freeze drying, 209 g of a light brown powder were obtained. This product was then intensively mixed at room temperature in an atmosphere of inert gas with the CO₂ extract previously obtained, thus yielding 379 g of hop extract. The analysis of the latter is given in the following table: 10 15

TABLE 1

| Determination | Unprocessed Hops | Extract | Hops after water extraction |
|----------------------|------------------|---------|-----------------------------|
| Water content % | 9.9 | 13.2 | 5.33 |
| Total resin % | 13.9 | 33.2 | 2.1 |
| Total soft resins % | 12.6 | 30.8 | 1.4 |
| 25 α -acids % | 5.2 | 13.8 | <0.1 |
| β -acids % | 7.4 | 17.0 | 1.4 |
| Hard resins % | 1.3 | 2.4 | 0.7 |
| Tannins % | 4.1 | 3.8 | <0.1 |

- 30 2. 1 kg of air-dry Hallertau hops were processed in the installation under the following conditions with dry CO₂:

Mixture separation temperature $t_2=45^\circ\text{C}$.

Result:

110 g of a substantially anhydrous, olive green, pasty extract were obtained. The residue of extracted hops was yellowish light green in colour and almost odourless. Analysis is shown in the following table: 40

Extraction pressure $p_1=400$ atmospheres gauge.

Mixture separation pressure $p_2=60$ at. gauge.

35 Extraction temperature $t_1=45^\circ\text{C}$.

TABLE 2

| Determination | Unprocessed Hops | Extract | Hops after CO ₂ extraction |
|---|------------------|---------|---------------------------------------|
| Water content % | 7.0 | < 1 | 6.9 |
| Total resins % | 14.5 | 98 | 3.6 |
| Total soft resins % | 12.7 | 87 | 1.5 |
| 45 α -acids % | 4.4 | 33.8 | under limit of detectability |
| 50 β -acids % | 8.3 | 53.2 | 1.5 |
| Hard resins % | 1.8 | 11 | 2.1 |
| Degree of extraction of α -acids % | | | 100 |
| 55 Degree of extraction of total resins % | | | 76 |
| Tannins % | 3.55 | < 0.1 | 4.2 |

- 60 3. 1 kg of air-dry Hallertau hops were processed in the installation with N₂O under the following conditions:

Mixture disintegration temperature $t_2=25^\circ\text{C}$. 65

Result:

150 g of a water containing, olive green, pasty extract were obtained. The residues of extracted hops was yellowish light green in colour and almost odourless. Analysis is shown in the following table: 70

Extraction pressure $p_1=200$ atmospheres gauge.

Mixture separation pressure $p_2=70$ at. gauge.

Extraction temperature $t_1=50^\circ\text{C}$.

TABLE 3

| Determination | Unprocessed Hops | Extract | Hops after N ₂ O extraction |
|---------------------|------------------|---------|--|
| 75 Water content % | 9.9 | 33 | 5.9 |
| Total resin % | 13.9 | 66.5 | 2.75 |
| Total soft resins % | 12.6 | 64.6 | 1.84 |
| α -acids % | 5.2 | 28.4 | 0.17 |
| β -acids % | 7.4 | 36.2 | 3.3 |
| 80 Hard resins % | 1.3 | 1.9 | 0.9 |
| Tannins % | 4.1 | < 0.1 | 4.5 |

WHAT WE CLAIM IS:—

1. A method of producing hop extracts from hops by extraction with a solvent, in which air-dry hops are extracted with a gas which is supercritical in respect of both pressure and temperature and which is unobjectionable from the health point of view, said gas comprising SF_6 , CHF_3 , CHF_2Cl , CF_3Cl , $\text{CF}_2=\text{CH}_2$, C_2F_6 , N_2O , ethane, ethylene, or CO_2 or mixtures of any two or more thereof, the extract being thereafter separated from the resulting solution by lowering the pressure to below the critical pressure.
2. A method according to Claim 1, wherein the entire soft resin fraction and the essential oils of the hops but less than 100% of the hard resin fraction are extracted by use of extraction pressures of from 100 to 220 atmospheres gauge.
3. A method according to Claim 1, wherein all the α -acids and also the essential oils, but less than 100% of the β -acids contained in the hops and less than 100% of the hard resin fraction, are extracted by use of extraction pressures of from 100 to 220 atmospheres gauge and by further separating the resulting extract by subjecting it to further supercritical extraction at pressures of 100—150 atmospheres gauge.
4. A method according to Claims 1 to 3, wherein the hops freed from resin components and essential oils by processing with the dry supercritical gas are thereupon subjected to a second extraction with moist supercritical gas the resulting extract being mixed with the products obtained from the extraction with the dry supercritical gas.
5. A method according to Claims 1 to 3 for producing a hop extract containing tannins, wherein the hops are extracted with a supercritical gas, the residue is extracted with water in a known procedure, the latter extract dried and mixed with the first extract obtained by extraction with supercritical gas.
6. A method according to any of Claims 1 to 5 for producing hop extracts which contain less than 2% water, wherein a temperature above the critical temperature is maintained during the separation.
7. A method according to Claim 1, wherein the pressure at which the extraction is conducted is from 150 atmospheres gauge to 400 atmospheres gauge.
8. A method according to Claim 1, wherein the temperature at which the extraction is conducted is between 40°C and 50°C .
9. A method according to Claim 1 substantially as hereinbefore described with reference to the accompanying drawing.
10. A method according to Claim 1 substantially as described in any one of the Examples.
11. A hop extract whenever produced by a method according to any one of the preceding Claims.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.



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